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Title: Polymer Equations of State and Shock-Driven Decomposition

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Polymer Equations of State and Shock-Driven Decomposition

Josh Coe

Physics & Chemistry of Materials (T-1)
Los Alamos National Laboratory

November 14, 2018

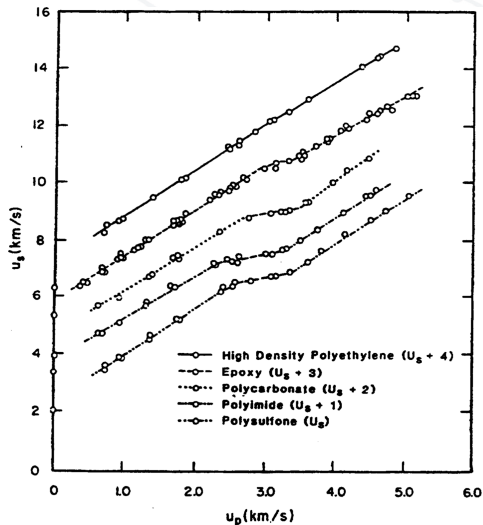
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Quick Outline

- Polymers decompose under shock loading
 - Experimental evidence
- EOS Modeling approaches
 - SESAME
 - Thermochemical
- Detailed application to foams: polyurethane
- Some hydrodynamic implications of EOS choices: epoxy
- Adding kinetics: polysulfone

Polymer Hugoniot Display Structure

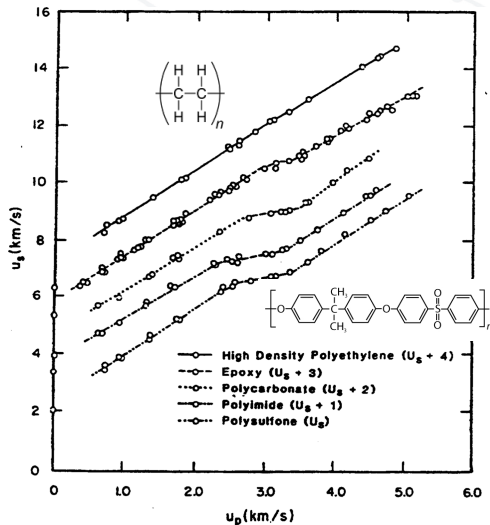
- Derivative discontinuities at $u_p \sim 3$ km/s (typically $P \sim 25$ GPa)
- Volume collapse in $P-V$



LA-13006-MS, LANL (originally prepared in 1977)

Polymer Hugoniot Structure

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- Volume collapse in P - V
 - Degree of collapse correlates qualitatively with chemical structure

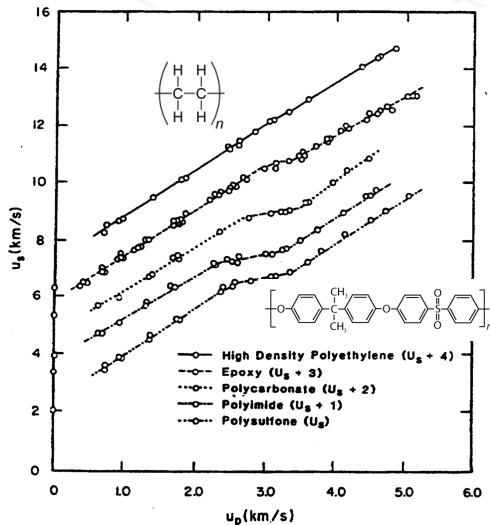


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Polymer Hugoniot Structure

- Derivative discontinuities at $u_p \sim 3$ km/s (typically $P \sim 25$ GPa)
- Volume collapse in $P-V$
 - Degree of collapse correlates qualitatively with chemical structure
 - Interesting and important stuff at lower u_p , won't discuss



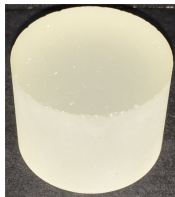
LA-13006-MS, LANL (originally prepared in 1977)

Hugoniot Structure: Two Early Views

- Phase transition (LANL, 1977)
 - analogous to graphite→diamond
 - “compression...is two-dimensional in nature” below the transition, “more typical of a three-dimensional solid” above

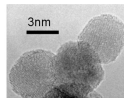
Hugoniot Structure: Two Early Views

- Phase transition (LANL, 1977)
 - analogous to graphite→diamond
 - “compression...is two-dimensional in nature” below the transition, “more typical of a three-dimensional solid” above
- Decomposition (LLNL, 1979)
 - “..hydrocarbons at high pressure ($\gtrsim 10$ GPa) and high temperature ($\gtrsim 1000$ K) dissociate into carbon in the diamond phase and hydrogen in a condensed molecular phase”



epoxy

Smack! →

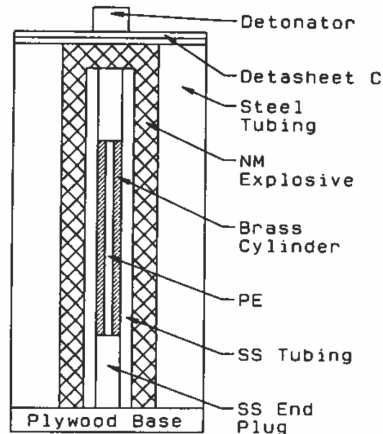


carbon+H₂O+CO+CO₂+...

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Hugoniot Structure: Recovery Experiments

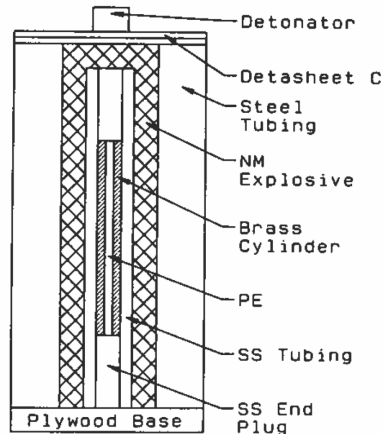
- Experiments on polyethylene and Teflon
- Setup
 - Single-shock, Mach compression
 - Hermetically-sealed capsule
 - Enabled recovery of soot and gases
 - Mass spectrometry, XRD, TEM



PE: SCCM-1989, p. 687; PTFE: *J. Chem. Phys.* **80**, 5203 (1984)

Hugoniot Structure: Recovery Experiments

- Experiments on polyethylene and Teflon
- Setup
 - Single-shock, Mach compression
 - Hermetically-sealed capsule
 - Enabled recovery of soot and gases
 - Mass spectrometry, XRD, TEM
- Polyethylene results
 - Polymer recovered at ~ 20 GPa
 - Gases and soot recovered 28-40 GPa
 - Gases were $>80\%$ mol CH_4 and H_2
 - Soot was neither graphite nor diamond



PE: *SCCM-1989*, p. 687; PTFE: *J. Chem. Phys.* **80**, 5203 (1984)

Unreactive EOS: SESAME Framework

- Purely hydrostatic, no strength or viscoelasticity
- 3-part decomposition of free energy

$$F(\rho, T) = \phi(\rho) + F_{\text{ion}}(\rho, T) + F_{\text{elec}}(\rho, T)$$

- Methods to incorporate equilibrium phase boundaries

Unreactive EOS: SESAME Framework

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- Methods to incorporate equilibrium phase boundaries
- We apply this to just about everything
 - High explosive products being the exception

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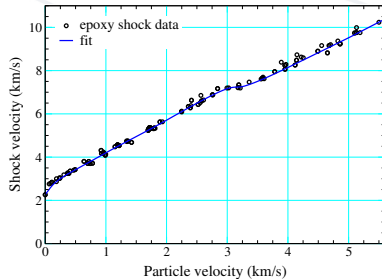
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$$F(\rho, T) = \phi(\rho) + F_{\text{ion}}(\rho, T) + F_{\text{elec}}(\rho, T)$$

- Methods to incorporate equilibrium phase boundaries
- We apply this to just about everything
 - High explosive products being the exception
- With regards to polymers:
 - Electronic part not that important $\rho/\rho_0 \lesssim 3$
 - Ionic models of Mie-Grüneisen form (variations on Debye)
 - Cold curve extracted from fit to shock data

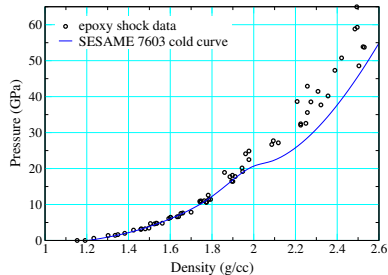
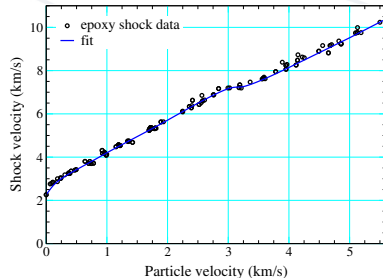
Our Traditional Approach to Polymer EOS

- Fit some shock data



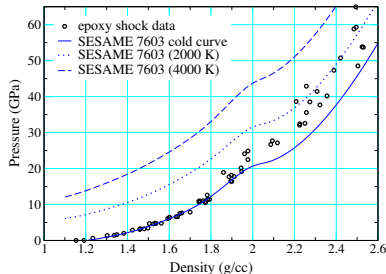
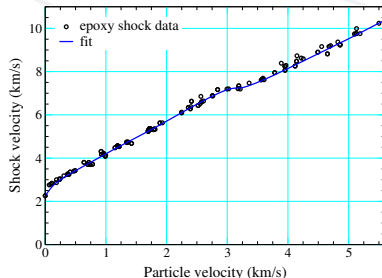
Our Traditional Approach to Polymer EOS

- Fit some shock data
- Assume some characteristic temperature
 - Cold curve by subtraction



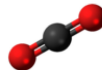
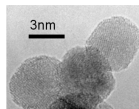
Our Traditional Approach to Polymer EOS

- Fit some shock data
 - Assume some characteristic temperature
 - Cold curve by subtraction
- Potential problems:
 - Structure present even at 0K
 - Structure preserved to high T
 - Completely reversible transition
- Thermals often poorly constrained
 - Important for foams



Thermochemical Modeling

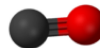
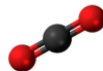
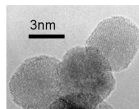
- Decomposition products as mixture of fluids and bulk solids
 - Each constituent has its own free energy model
 - Fluids: spherical, pairwise interaction potential translated to free energy with perturbation theory
 - Solids: SESAME model
 - Mixture rule required (non-unique)



carbon+H₂O+CO+CO₂+...

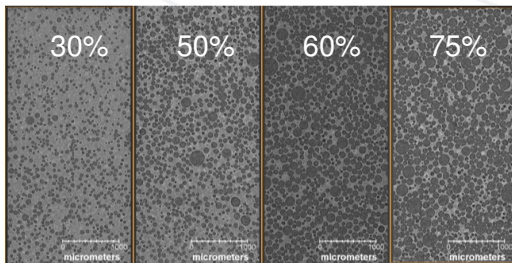
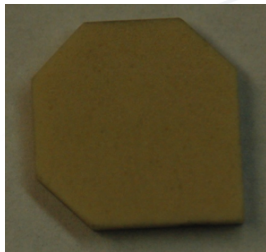
Thermochemical Modeling

- Decomposition products as mixture of fluids and bulk solids
 - Each constituent has its own free energy model
 - Fluids: spherical, pairwise interaction potential translated to free energy with perturbation theory
 - Solids: SESAME model
 - Mixture rule required (non-unique)
- Assume full thermodynamic (and thus, chemical) equilibrium
 - Adjust concentrations until minimal free energy found and stoichiometry preserved



carbon+H₂O+CO+CO₂+...

PMDI Polyurethane: Approach

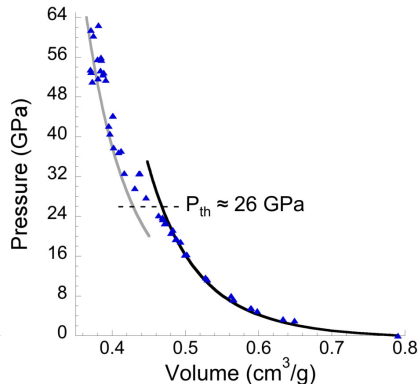
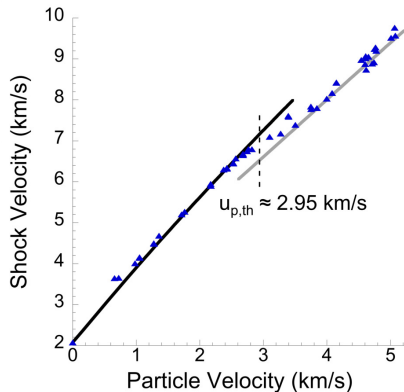


- Shock data for polyurethane at 0-75% porosity
- Thermochemical modeling above some threshold
 - Threshold varies with porosity, unknown a priori
 - Carbon as diamond for full density, as graphite for foams
 - Only adjustable parameter is E_0
- Reactants were SESAME + $P - \alpha$ porosity model
 - Only porous parameter is crush pressure, P_c

Dattelbaum, et al., *J. Appl. Phys.* **115**, 174908 (2014)

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PMDI Polyurethane: Full Density Results



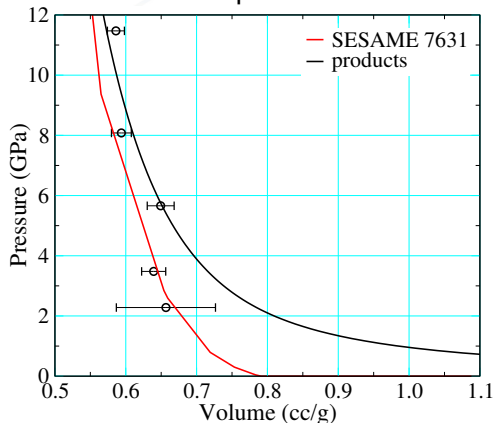
- E_0 of products adjusted to match data above transition
- Reactant EOS calibrated to all solid data
- Legacy EOS SESAME 7631 (shown in following)

Dattelbaum, et al., *J. Appl. Phys.* **115**, 174908 (2014)

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Polyurethane: Foamed Results

30% porous

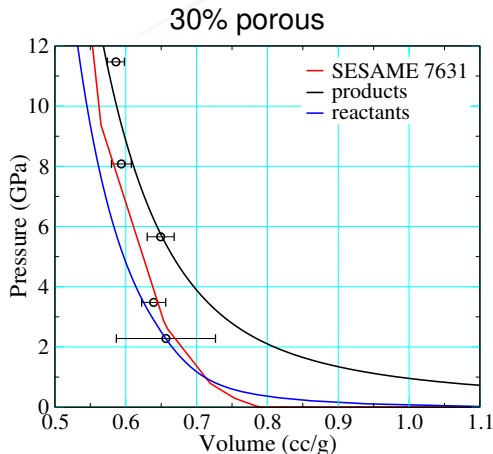


- Porous E_0 same as for solid
- Good agreement with highest points

Dattelbaum, et al., *J. Chem. Phys.* **115**, 174908 (2014)

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Polyurethane: Foamed Results

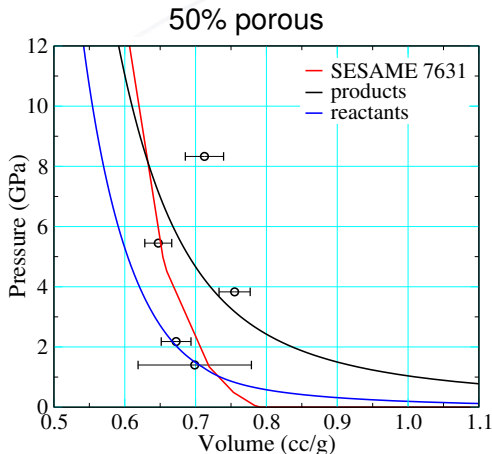


- Porous E_0 same as for solid
- Good agreement with highest points
- Set $P_c = 16$ kbar
- Yields product locus to right of reactants

Dattelbaum, et al., *J. Chem. Phys.* **115**, 174908 (2014)

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Polyurethane: Foamed Results

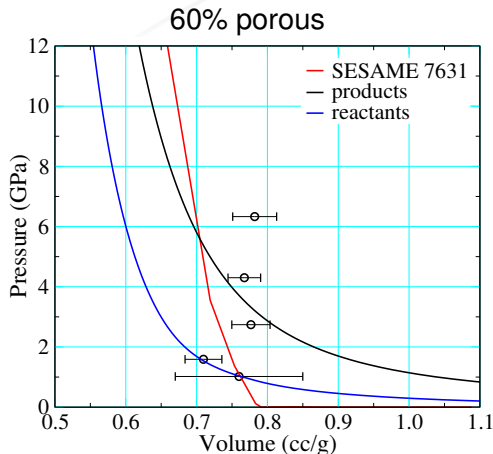


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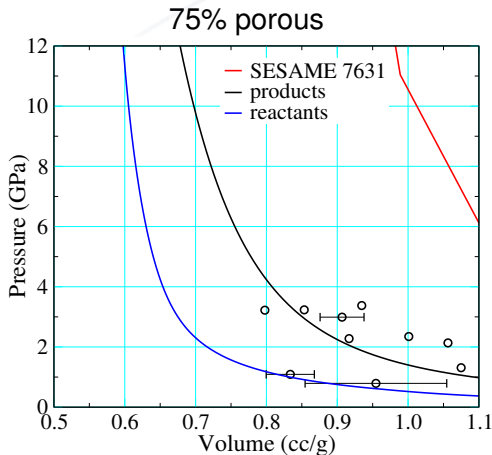


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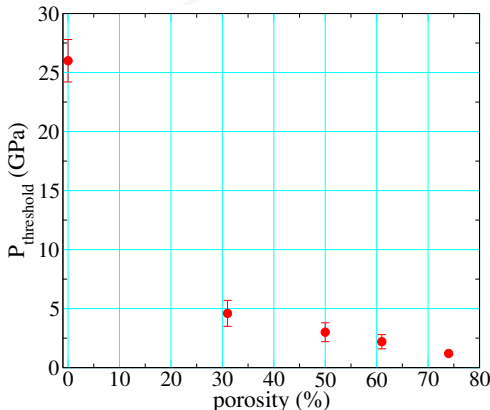


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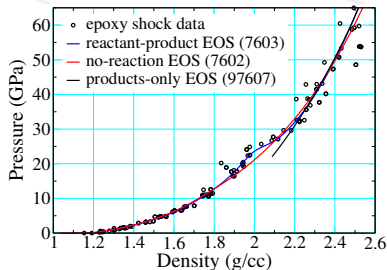
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- Yields product locus to right of reactants
- Experimental error bars should probably be larger
- Approach makes qualitative sense of the pattern
- Transition threshold drops dramatically with porosity

Dattelbaum, et al., *J. Chem. Phys.* **115**, 174908 (2014)

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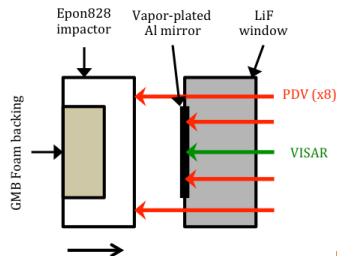
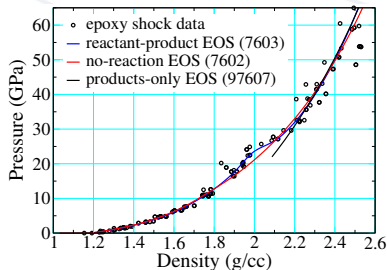
Hydrodynamic Implications: Shock and Deep Release

- Fredenburg TITANS thesis (LA-CP-16-06822)
- New products EOS 97607
- Historical EOS
 - 7603 includes structure in fit
 - 7602 excludes structure from fit



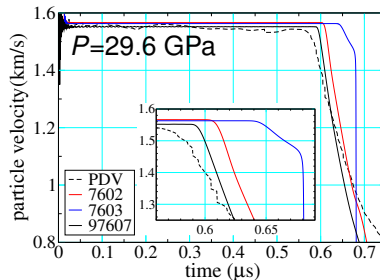
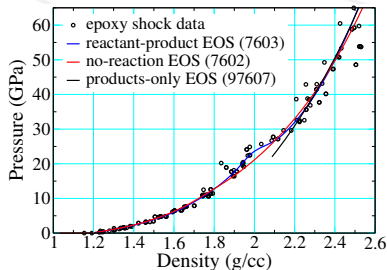
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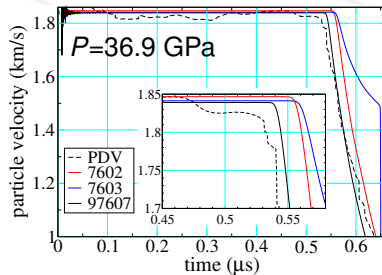


Hydrodynamic Implications: Shock and Deep Release

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- New products EOS 97607
- Historical EOS
 - 7603 includes structure in fit
 - 7602 excludes structure from fit
- Release experiment gives P and its first two ρ derivatives (c_S^2 and \mathcal{G})
 - Products give better c_S (8% error vs. 16% and 29%)
 - \mathcal{G} ok, better for higher P
 - multiwave structure from 7603

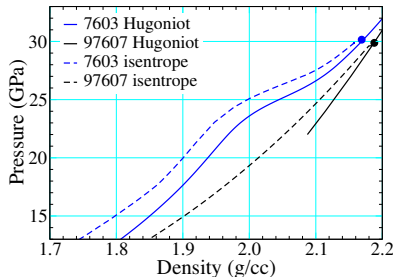
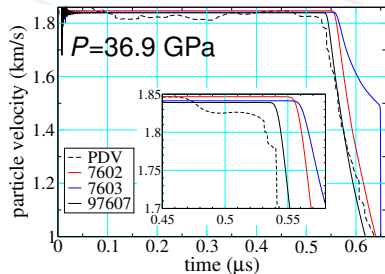


Reversible Transitions and Structured Release



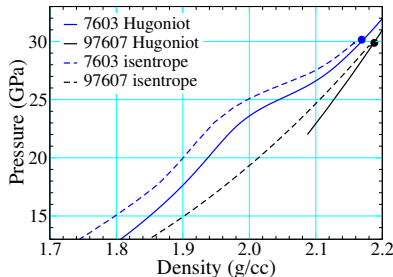
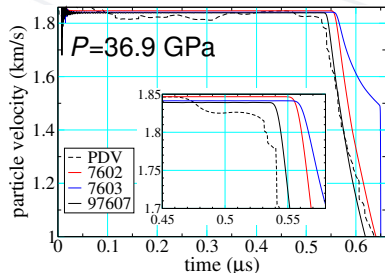
Reversible Transitions and Structured Release

- Hugoniot structure appears also in the isentropes
 - Release produces spurious “back-reaction”
 - Multiwave structure results
- Reversibility issue
 - Should we treat polymers more like HE, or metals?



Reversible Transitions and Structured Release

- Hugoniot structure appears also in the isentropes
 - Release produces spurious “back-reaction”
 - Multiwave structure results
- Reversibility issue
 - Should we treat polymers more like HE, or metals?
- When do we clearly *not* care?
 - Shocks below transition
 - Shocks well above transition
- Relevance dictated by strength of shock and timescale of interest



Adding Kinetics

- Using HE burn module in LANL's xRage code
- So far we've only tried an Arrhenius rate

$$\mathcal{R} = \frac{d\lambda}{dt} = (1 - \lambda)^n \nu e^{(-T_a/T)}$$

\mathcal{R} = reaction rate

λ = mass fraction of products

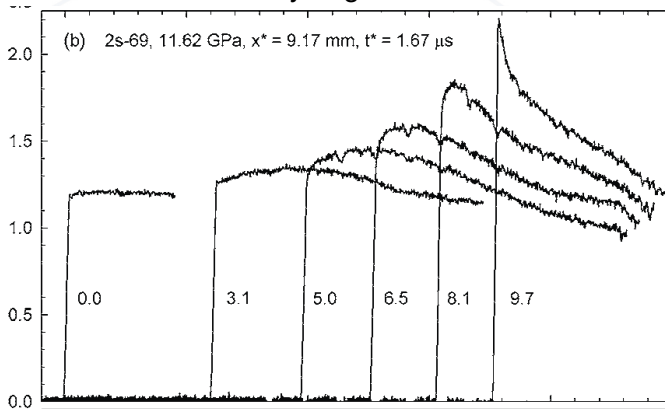
n = reaction order (parameter)

ν = frequency factor (parameter)

T_a = activation temperature (parameter)

Rate Model Calibration: Data

What you get in HE



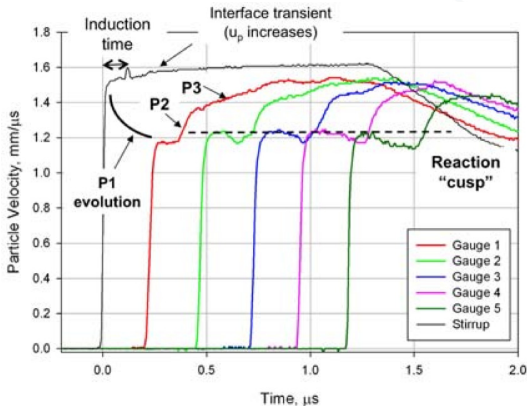
Embedded gauge data for PBX 9502

Gustavsen, et al., *J. Appl. Phys.* **99**, 114907 (2006)

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Rate Model Calibration: Data

What we'd *like to get* for polymers...



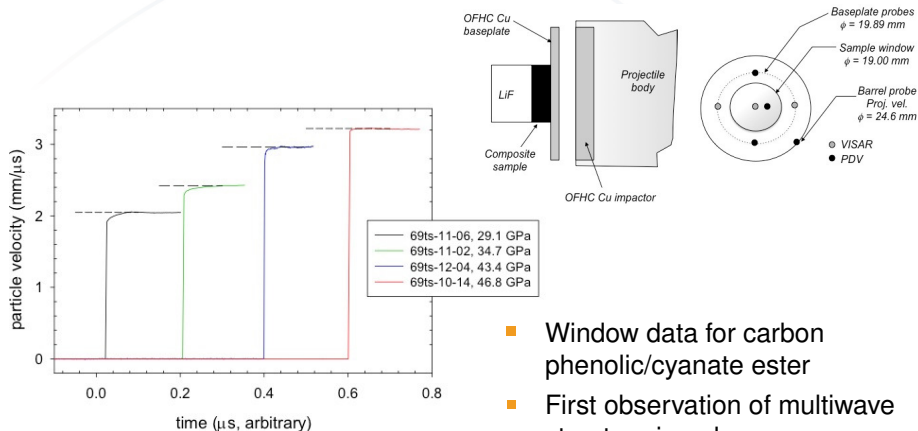
Embedded gauge data for phenylacetylene liquid

Dattelbaum & Sheffield, *AIP Conf. Proc.* **1426**, 627 (2012)

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Rate Model Calibration: Data

What we'd *actually gotten* for polymers (until very recently)...



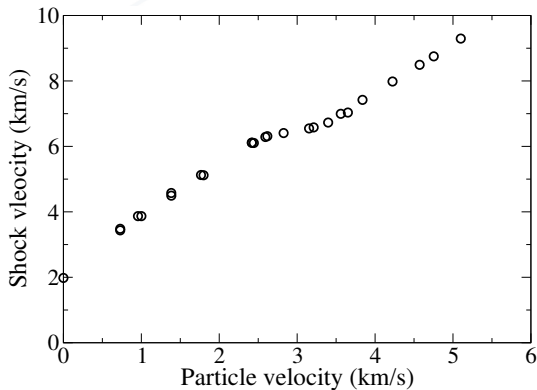
- Window data for carbon phenolic/cyanate ester
- First observation of multiwave structure in polymers

Dattelbaum, et al., *J. Appl. Phys.* **116**, 194308 (2014)

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Rate Model Calibration: Data

What we *usually have* for polymers...



Polysulfone shock data:

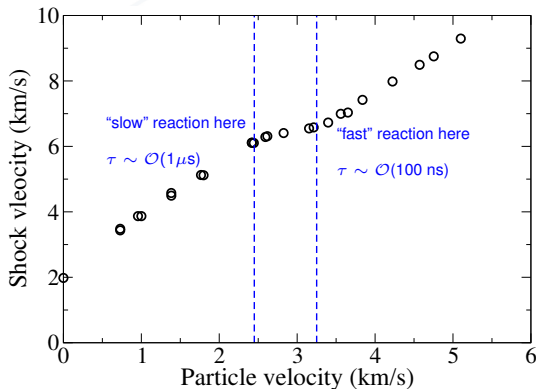
- Shock velocity from transit time (first wave arrival only)
- Particle velocity from impedance matching

Carter & Marsh, **LA-13006-MS** (1995)

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Rate Model Calibration: Data

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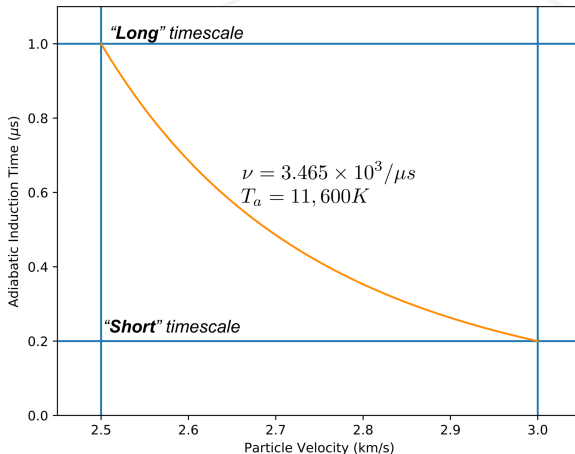
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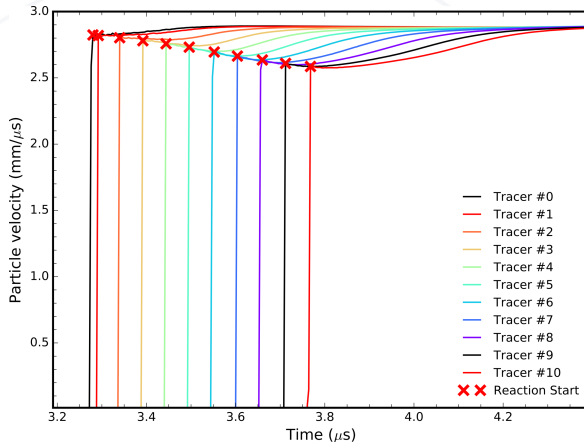
Rate Model Calibration: Practice



- Using $1/(\text{adiabatic induction time})$ as proxy for rate
- For a given pair of EOS:
 - T_a sets u_p range
 - ν shifts laterally

Simulated Wave Profiles in Polysulfone

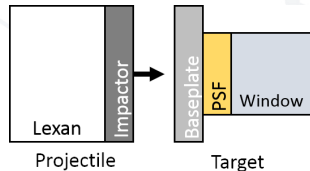
- $P_{\text{input}}=22.1$ GPa; transition starts ~ 18.5 GPa



- Qualitative features good, but experimental reaction signatures (P1 decay, P2 rise) much more subtle

Top Hat Experiments on Polysulfone

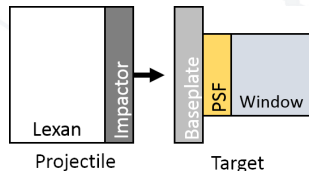
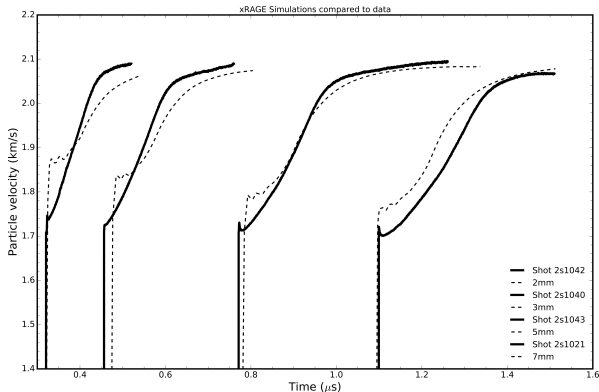
PDV at (reshock) interface with window



Top Hat Experiments on Polysulfone

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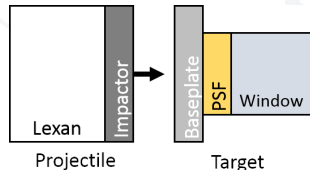
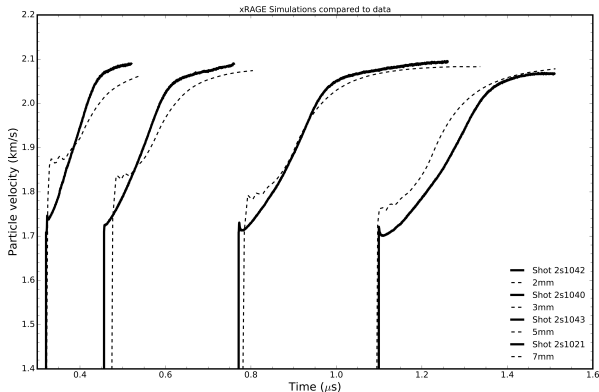
increasing sample thickness \rightarrow



Top Hat Experiments on Polysulfone

PDV at (reshock) interface with window

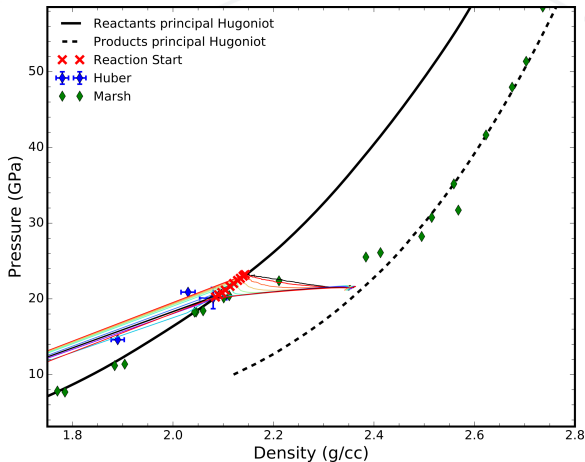
increasing sample thickness →



Simulation:

- underestimates total P1 decay
- exaggerates P1 variation with thickness
- P2 slow when thin, fast when thick

“Reaction Path” in Polysulfone



- P1 states relax along reactant Hugoniot
- All tracers ride P2 to products Hugoniot

Summary & Future Directions

- Polymers decompose under shock loading
 - $u_p \sim 3$ km/s, $P \sim 25$ GPa at full density
- Threshold conditions drop dramatically as porosity increases
 - Response may become anomalous
- Products modeled reasonably well under assumption of full thermodynamic equilibrium
- Treating reactants and products as single material can produce artifacts in hydrodynamic simulation
- Ongoing
 - Understanding the interaction of chemistry and flow
 - Work on polyethylene, polysulfone, SX358, polyimide...

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Extra Slides

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Thermicity coefficients and detonability

- In order to produce a self-sustaining wave, a material must have a positive thermicity coefficient

$$\sigma = \left(\frac{\partial P}{\partial \lambda} \right)_{V,E} = \frac{\Delta V}{V} - \frac{\Gamma}{c^2} \Delta H$$

σ = thermicity coefficient

λ = reaction progress variable

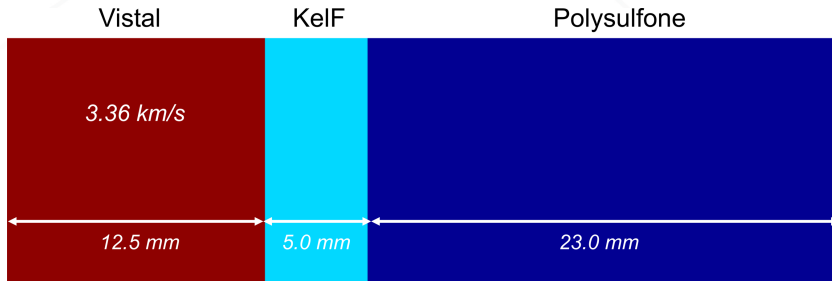
Γ = Grüneisen parameter

c = frozen sound speed

ΔH = enthalpy (confusingly, also called reaction thermicity)

- Exothermic decomposition does not guarantee detonation

Setup for wave profile run



Rate Model Calibration: Theory

- Adiabatic induction time for constant-volume burn

$$t_{\text{ad}}(T_0) = \frac{T_0^2}{\nu T_a (T_1 - T_0)} e^{(T_a/T_0)}$$

T_0 = reactant temperature

T_1 = product temperature

ν = frequency factor (parameter)

T_a = activation temperature (parameter)

- In our case, these are Hugoniot temperatures
- There's a problem when reaction lowers temperature
- Because $T_0 = T_0(u_p)$, we'll consider $t_{\text{ad}}(u_p)$

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